

Direct determination of the lipid content in starch–lipid composites by time-domain NMR[☆]

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Abstract

Starch–lipid composites, prepared by excess steam jet cooking aqueous mixtures of starch and lipid, are used in a broad range of applications for which their performance can depend upon accurately knowing the amount of the lipid contributed by the composites. A rapid and non-destructive method based on time-domain nuclear magnetic resonance spectroscopy (TD-NMR) was evaluated to quantitate soybean oil (SBO) or butterfat (BF) content in a series of dried starch–lipid composites. Transverse hydrogen relaxation (T_2) properties of the composites were examined using Carr, Purcell, Mieboom, Gill (CPMG) pulse experiments and multi-exponential decay fitting routines were utilized to evaluate the various components. Spin–echo TD-NMR experiments were used to quantitate the amount of lipid in the composites and agreed well with lipid extraction experiments ($R^2 = 0.998$). Moisture levels in the composites were also simultaneously determined and compared reasonably well to moisture levels determined gravimetrically ($R^2 = 0.881$). TD-NMR was shown to be a rapid method to determine lipid and moisture content in these starch–lipid composites without the need for labor intensive extraction and gravimetric methods currently employed.

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1. Introduction

Steam jet cooking is a convenient and inexpensive process utilized to prepare aqueous starch dispersions for industrial applications (Klem and Brogley, 1981). As part of our research on the utilization of renewable raw materials such as starch and vegetable oils,

an interesting class of highly stable, water dispersible, starch–lipid composites have been developed by co-jet cooking mixtures of starch and lipophilic materials such as vegetable oils under excess steam conditions (Knutson et al., 1996; Eskins and Fanta, 1997, 1999; Fanta et al., 1999). The resulting composites can readily contain 50 wt% lipophilic material relative to the starch component, are water dispersible over a wide range of dilution, and are currently being examined for use in a broad range of food and non-food applications such as lubricants (Biresaw et al., 2007), meat patties (Garzon et al., 2003), and soft serve ice cream (Byars, 2002). Microscopic analyses have shown the composites to consist of 1–10 μm diameter lipid droplets coated with a thin

[☆] Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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film of firmly bound starch at the lipid–water interface (Fanta and Eskins, 1995; Eskins et al., 1996; Fanta et al., 1999). The water dispersed starch–lipid composites can be drum dried and milled to produce powders of the composites that are easily reconstituted in water to again form smooth stable dispersions.

Starch–SBO composites have been examined by Knutson et al. (1996) to determine the amount of oil incorporated into the composites and evaluate whether the jet cooking/drum drying altered the chemical composition of either the starch or the oil. Although their study concluded that no chemical reactions between the SBO and starch had occurred within the composites to covalently link them, they discovered a portion of the SBO was held quite tenaciously in the dried composites. A variety of extraction techniques and conditions were examined in an effort to remove the SBO from the composite. The extraction conditions ranged from room temperature and Soxhlet extraction using various organic solvents to a two step hydrolysis/extraction procedure, whereby, the starch matrix was first digested by α -amylase to release the composite's SBO followed by oil recovery with hexane. Eight repetitive room temperature or Soxhlet extractions recovered only a fraction (52–82%) of composite's total SBO compared to the more labor intensive starch hydrolysis/extraction procedure. Furthermore, the starch hydrolysis/extraction experiments showed a substantial portion of the initial SBO (16–23%) introduced during the composite preparation was missing from the composites and was attributed to losses that occurred during the jet cooking and drum drying operations.

From the above work, one can appreciate not only the inherent difficulties in preparing starch–lipid composites with well defined oil amounts, but also the difficulties related to accurately determining their oil content by conventional extraction techniques. Because the quality and performance of applications utilizing these starch–lipid composites depend, in part, upon accurately knowing the amount of oil contained within the composites, a method to quickly and accurately determine the oil contained within these composites without resorting to labor intensive extractions is highly desirable.

To address these issues, we sought to use TD-NMR as a quick non-destructive method to quantitate the lipid content in these starch–lipid composites prepared by excess steam jet cooking. TD-NMR was introduced approximately 35 years ago, and the advent of hardware and software improvements has helped TD-NMR rapidly grow into a useful analytical tool in the polymer,

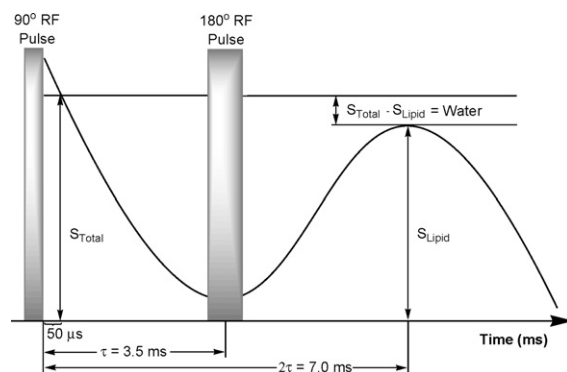


Fig. 1. The spin–echo NMR pulse sequence experiment used for lipid and moisture determination.

petroleum, pharmaceutical, agricultural, and food industries (Todt et al., 2001).

TD-NMR capitalizes on the differing relaxation times of hydrogen nuclei contained in the solid or liquid phases of the material being examined (Ruan and Chen, 1998), and spin–spin transverse relaxation times, T_2 , can be readily measured using CPMG pulse sequences (Meiboom and Gill, 1958). The T_2 for solids such as carbohydrate and protein, reduced mobility (i.e. so-called bound) water, and oil liquid components, are typically on the order of microseconds, a few milliseconds, and a few hundreds of milliseconds, respectively (Srinivasan, 1979; Gambhir, 1992; Ruan and Chen, 1998; Choi and Kerr, 2003). Additionally, the use of spin–echo pulse sequence, like that shown in Fig. 1, allow the solid and liquid components to be determined when appropriate calibration standards are implemented.

Herein, dried starch–lipid composites containing varying amounts of either soybean oil (SBO) or butterfat (BF) were prepared by excess steam jet cooking and subsequently examined by TD-NMR using CPMG and spin–echo pulse sequences. The main objective of this work was to evaluate the ability of TD-NMR to quickly and accurately determine the amount of lipid contained in these starch–lipid composites. Additionally, because the starch–lipid composites typically contain low amounts of moisture after drying that can influence the shelf life and stability of the starch–lipid composites, TD-NMR spin–echo pulse sequence experiments were used to simultaneously examine the water content contained in these composites. The implementation of TD-NMR to quickly determine the oil and moisture content in these starch–lipid composites using TD-NMR will allow us to better characterize and tailor composite properties for applications that utilize these composites.

2. Materials and methods

2.1. Materials

All chemicals were used without further purification unless otherwise noted. Kroger brand soybean oil and butter (butter moisture content = 17.7%, as determined by AOCS method Ca 2c-25) were purchased from a local supermarket. Waxy cornstarch (Waxy No. 1, moisture content = 11.1%) and normal dent cornstarch (Normal, moisture content = 9.70%) were obtained from A.E. Staley Mfg. Co. (Decatur, IL). Deionized water was used for the preparation of all starch–lipid composites. Chloroform, methanol, α -amylase Type VIII-A obtained from barley malt, and all other chemicals were purchased from Sigma–Aldrich Chemical Company (Milwaukee, WI).

2.2. Representative starch–lipid composite preparation (10.9% SBO–waxy starch composite)

In a typical preparation, a mixture of waxy starch (450.2 g, moisture content approximately 11.1%) was added to deionized water (3000 ml) and stirred in a 4000 ml stainless steel Waring blender (model 37BL84; Dynamics Corporation of America, New Hartford, CT). The resulting slurry was delivered to the jet cooker utilizing a Moyno progressing cavity pump (Robbins Meyers, Springfield, OH) at a flow rate of about 1 l/min. The starch slurry and steam were combined in a Penick and Ford hydroheater (Penford Corp., Cedar Rapids, IA). Cooking temperature was 140 °C using steam supplied at 550 kPa (65 psig), and the hydroheater backpressure set at 377 kPa (40 psig). Four thousand milliliters of the cooked starch solution (solids content: 9.78%, as determined by freeze-drying accurately weighed amounts of the dispersion in duplicate) was collected. The solids content of the collected starch solution varied because of dilution of the cooked dispersion with condensed steam. To a portion of the starch solution (3003.5 g, contains 293.7 g starch), SBO (35.85 g) was added and the mixture blended at high speed in a Waring blender for approximately 2 min. This oil–starch suspension was then fed through the jet cooker under the conditions previously described. A center cut (approximately 2500 ml) of the white opaque dispersion was collected from the jet cooker and subsequently drum dried on a pilot-scale double drum dryer (model 20; Drum Dryer and Flaker Company, South Bend, IN) heated with steam at 308 kPa (30 psig) (135 °C) to give white composite flakes. The flakes were subsequently milled to a fine powder using an ultra centrifugal mill (Model ZM 200; Retsch Inc.,

Newtown, PA) operating at 300 Hz (18,000 rpm). The theoretical oil concentration in the composite was 10.9%.

2.3. Representative procedure to determine lipid content in composites by α -amylase starch digestion/solvent extraction

In a typical procedure, a smooth dispersion of waxy starch–SBO composite (5.9185 g; moisture content = 1.86%, SBO content = 0.6331 g, 10.9% in composite) in 20 mM of pH 6.9 phosphate buffer containing 6.7 mM NaCl (50 ml) was prepared in an Erlenmeyer flask by magnetically stirring the mixture for approximately 5 min. To the dispersion α -amylase (152.3 mg) was added and the mixture stirred a few minutes to disperse the α -amylase. The flask was then placed into a shaking water bath at 37 °C and shaken at 1.7 Hz (100 rpm) for 20 h. After the designated reaction time, the room temperature reaction mixture was transferred to a separatory funnel using 2:1 CHCl_3 :MeOH (100 ml). The funnel was shaken to partition lipid into the organic phase. The organic phase was removed and the aqueous phase was further extracted with CHCl_3 (2 \times 50 ml) and the organic phases combined. The organic phase was washed with saturated brine (1 \times 50 ml) and then dried with Na_2SO_4 . The organic extracts were filtered under vacuum through a fine glass frit filter and the solvent removed at 30 °C *in vacuo*. The residue weight was recorded and then the residue dried in a vacuum oven at 36–40 °C until residue weight was constant and did not change with further drying. A yellow oil (0.6059 g, 95.7% of theoretical oil content) was collected.

2.4. Gravimetric determination of moisture in composites by freeze-drying

The weight loss on drying of the starch–lipid composites (moisture content) were gravimetrically determined by freeze-drying using a Labconco FreeZone 4.5 L Freeze Dry System (Kansas City, MO) maintained at –53 °C and 0.0006 kPa. Samples (3–4 g) were dried to constant weight over 24–48 h. Moisture determinations for all samples were performed in duplicate or triplicate.

2.5. Time-domain nuclear magnetic resonance

TD-NMR experiments were carried out using a Bruker Minispec MQ20 NMR Analyzer operating at a resonance frequency of 19.98 MHz and a 180-mm absolute probe head maintained at 40.0 ± 0.1 °C. NMR tubes (18 mm diameter) were filled to 28 mm with composite samples. The tubes were stoppered and sealed

with parafilm to limit changes in sample composition. All calibration and sample measurements were made at 40.0 °C. Transverse (T_2) relaxation times in the millisecond time domain were determined using CPMG pulse sequence experiments. Acquisition parameters were set to a 90° pulse of 3.74 μ s and a 2 s recycle delay between scans. The echo time (τ) was 250 μ s and a total of 64 scans and 2048 echoes were collected for each sample. Measurements were repeated in triplicate and averaged. The transverse relaxation curves were analyzed using the biexponential or triexponential decay fitting routines, Eqs. (1) and (2), respectively, in OriginPro version 7.5 (OriginLab Corp., Northampton, MA) to determine discrete T_2 values. In these equations, A_0 , A_1 , A_2 , and A_3 are pre-exponential weighting factors, t =time, and T_{2a} , T_{2b} , and T_{2c} are the time constants:

Biexponential :

$$A = A_0 + A_1 \exp\left(-\frac{t}{T_{2a}}\right) + A_2 \exp\left(-\frac{t}{T_{2b}}\right) \quad (1)$$

Triexponential :

$$A = A_0 + A_1 \exp\left(-\frac{t}{T_{2a}}\right) + A_2 \exp\left(-\frac{t}{T_{2b}}\right) + A_3 \exp\left(-\frac{t}{T_{2c}}\right) \quad (2)$$

Spin-echo acquisition parameters used were set to a 90° pulse of 3.14 μ s using a 90–180° pulse spacing (τ) of 3.5 ms with a 180° pulse of 6.28 μ s. A 2 μ s recycle delay between scans was used and a total of 32 scans were collected for each sample. Samples were thermally equilibrated to 40 °C in heating blocks for 15 min prior to NMR analysis. Measurements for each composite were run on three samples and each sample was run in triplicate to verify reproducibility and achieve greater precision.

Eleven SBO calibration standards ranging from 0.5 to 38% SBO were prepared by suspending accurately weighed amounts of SBO onto accurately weighed amounts of milled, jet cooked drum-dried waxy starch. The 11 SBO standards were measured using the spin-echo pulse sequence described above and analysis of the data points gave the linear equation: $y = 0.4249x + 0.0102$ ($R^2 = 0.9999$). BF content in the starch-BF composites were determined similarly using five calibration standards ranging in BF from 2 to 39%. Analysis of the BF calibration data gave the linear equation: $y = 0.8459x - 0.3442$ ($R^2 = 0.9996$).

Moisture calibration curves for the starch-SBO composites were obtained using a starch-SBO composite for which the moisture content was determined gravimetrically by freeze-drying. A weight variation technique was used to prepare the moisture calibration curve, whereby the quantity of moisture detected by the NMR is varied by changing the height to which the sample tubes are filled with calibrant (Rubel, 1994). Six calibration standards were measured in the range from 0.90 to 6.0% moisture. Moisture content in the starch-BF composites was determined similarly using six standards. Analysis of the moisture calibration data gave linear equations: $y = 0.5526x + 0.0695$ ($R^2 = 0.9997$) and $y = 0.7436x + 0.1475$ ($R^2 = 0.9984$) for moisture in the starch-SBO and starch-BF composites, respectively.

3. Results and discussion

3.1. Starch-lipid composite preparation

A series of dried starch-SBO and starch-BF composites based on waxy and normal cornstarch were successfully prepared by excess steam jet cooking and drum drying. As shown in Table 1 (column 2), the theoretical amount of SBO or BF contained in these composites, based on the initial starch and lipid utilized to prepare the composites, ranged between 9 and 36 wt% and represents lipid loads typically found in applications utilizing the starch-lipid composites. During preparation of these composites, care was taken to control the lipid and starch ratios when jet cooking so the lipid percentages contained within the composites would be confidently known. Analyses of aqueous dispersions of the starch-lipid composites by light microscopy (data not shown) showed the typical 1–10 μ m diameter droplets of SBO or BF that did not coalesce over time. Drum drying and milling the aqueous dispersions of starch-lipid composites gave flowable powders that readily dispersed into water using a Waring blender. Other physical characteristics of these starch-lipid composites were similar in all major aspects to composites routinely prepared in our laboratories (Fanta et al., 1999).

3.2. Determination of composite's lipid content and moisture level

To evaluate the TD-NMR technique used to determine the composite's lipid and moisture content, the composite's total lipid and moisture contents were first determined using extraction and evaporation techniques,

Table 1

NMR, extraction and moisture data for various starch–lipid composites prepared by excess steam jet cooking

Starch–lipid composite ^a	Percent lipid in composite			Percent moisture in composite	
	Theoretical	Extraction	TD-NMR	Freeze-drying	TD-NMR
1 (waxy/SBO)	10.9	10.21 ± 0.04	10.14 ± 0.00	3.34 ± 0.02	3.59 ± 0.06
2 (waxy/SBO)	24.1	23.53 ± 0.20	24.08 ± 0.06	4.49 ± 0.11	4.45 ± 0.05
3 (waxy/SBO)	33.5	30.89 ± 0.29	31.78 ± 0.19	3.94 ± 0.01	4.37 ± 0.03
4 (normal/SBO)	10.7	9.85 ± 0.65	10.40 ± 0.08	4.38 ± 0.08	3.15 ± 0.04
5 (normal/SBO)	25.3	23.18 ± 0.81	23.57 ± 0.17	8.14 ± 0.01	7.19 ± 0.02
6 (normal/SBO)	35.5	33.40 ± 0.41	34.54 ± 0.11	2.12 ± 0.02	2.79 ± 0.03
7 (waxy/BF)	9.1	9.39 ± 0.05	10.49 ± 0.02	3.65 ± 0.51	3.14 ± 0.06
8 (waxy/BF)	16.8	17.05 ± 0.22	17.84 ± 0.16	3.05 ± 0.02	4.26 ± 0.03
9 (waxy/BF)	23.1	22.33 ± 0.49	23.65 ± 0.06	3.01 ± 0.08	4.34 ± 0.09
10 (normal/BF)	9.1	9.55 ± 0.43	10.44 ± 0.06	5.07 ± 0.56	5.33 ± 0.15
11 (normal/BF)	13.5	13.47 ± 0.47	15.29 ± 0.08	3.54 ± 0.08	4.18 ± 0.12
12 (normal/BF)	16.8	15.73 ± 0.20	17.44 ± 0.04	5.55 ± 0.12	6.31 ± 0.06
13 (normal/BF)	23.1	25.38 ± 0.33	26.13 ± 0.17	4.10 ± 0.34	4.99 ± 0.08

^a Waxy = waxy cornstarch; normal = normal dent cornstarch; SBO = soybean oil; BF = butterfat.

respectively. Because of the difficulty in fully extracting lipid from the composite, the starch matrix was first digested using α -amylase at 37 °C to release the SBO or BF from the composite structure. The freed lipid coalesced on the surface of the aqueous reaction media, and was subsequently extracted from the mixture using 2:1 (v/v) CHCl_3 :MeOH followed by additional CHCl_3 extractions. The amount of lipid determined in the composites by extraction, as shown in Table 1 (column 3), was consistent to the theoretically expected amount of lipid contained in the composites. These extraction results show that composites with well defined lipid contents can be readily prepared by excess steam jet cooking which is in contrast to Knutson's (Knutson et al., 1996) findings, whereby, large amounts (16–23%) of the starting SBO were lost during the jet cooking and drum drying processes.

Accurate determination of moisture content in various materials is challenging, and results can vary greatly depending upon the analytical method utilized (Rückold et al., 2001; Thiex and Richardson, 2003). For this study, the moisture contained in the composites, for which the TD-NMR moisture results were compared, was determined by weight loss upon freeze-drying. As shown in Table 1 (column 5), the starch–lipid composites had relatively low moisture levels ranging between 3 and 8%. The low moisture levels, typical for these composites after drum drying, is also beneficial for the TD-NMR approach as measurement of moisture levels beyond 10–15% by TD-NMR become problematic because the water is no longer strongly bound within the matrix and interferes with lipid determination (Todt et al., 2006).

3.3. Transverse T_2 relaxation determination of the composite from CPMG experiments

Transverse magnetization decay curves of the starch–lipid composites were obtained from CPMG experiments and a typical curve for the starch–SBO composites is illustrated in Fig. 2 (the curves for the starch–BF composites are similar). Because of the heterogeneous nature of the starch–lipid composites, it was expected that multi-exponential relaxation behavior of the lipid and water species might be observed. Accordingly, analyses of the curves for the starch–SBO

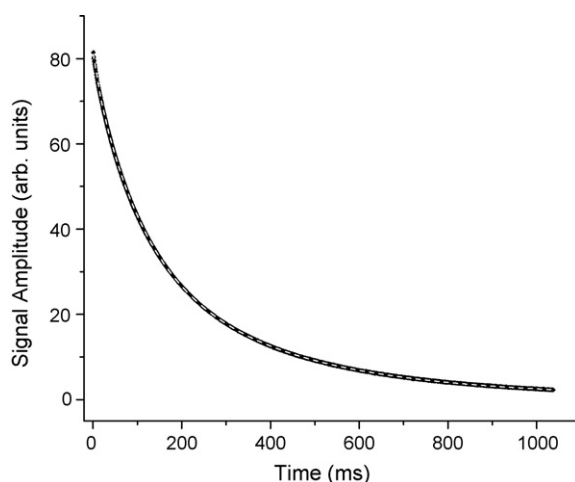


Fig. 2. A typical free induction decay (FID) signal for starch–SBO composites containing approximately 31 wt% oil in the composite. T_2 components are determined by fitting the data to a triexponential decay function (dashed line). The T_2 values determined for this FID data are 14.8, 101.3, and 328.1 ms. Starch–BF composites have similar curves.

composites showed the curves were best resolved into three exponential decaying components using Eq. (2), where T_{2a} , T_{2b} , and T_{2c} , of 15.7 ± 0.8 , 98.4 ± 5.2 , and 320.4 ± 14.0 ms, respectively (average $n = 3$, $R^2 = 0.9999$). Analyses of the starch–BF composites also showed three T_{2a} , T_{2b} , and T_{2c} components of 10.6 ± 2.4 , 87.2 ± 1.7 , and 246.0 ± 3.5 ms, respectively (average $n = 3$, $R^2 = 0.9998$).

To further understand the T_2 components observed in the starch–SBO composites, the T_2 of the neat SBO used in the composites was examined. The neat SBO relaxation curves were best resolved into two exponential decaying components using Eq. (1) having $T_{2a\text{SBO}}$ and $T_{2b\text{SBO}}$ of 102.6 ± 1.5 and 315.3 ± 3.4 ms, respectively. Presuming the SBO in the composites behaves similarly to the neat SBO and because the T_2 for SBO agree closely to those observed for the starch–SBO composites, T_{2b} (98.4 ± 5.2 ms) and T_{2c} (320.4 ± 14.0 ms), T_{2b} and T_{2c} observed for the starch–SBO composites were tentatively ascribed to lipid components. Recently, Hickey et al. (2006) have examined the T_2 in a potato chip samples containing canola oil using TD-NMR and observed a 57 and 208 ms T_2 they assigned to various canola oil components. The remaining short T_{2a} observed in the starch–SBO composites is likely due to water bound within the starch matrix, and was attributed to reduced mobility (i.e. so-called bound) water. This appears to be a reasonable presumption as T_2 for the multiphase behavior of water in similar solid matrices such as flour dough, bread, and starch has been reported in the range of 0.4–54 ms (Leung et al., 1983; D'Avignon et al., 1990).

3.4. Determination of composite lipid and moisture from spin–echo experiments

The moisture and lipid amounts contained in the composites were examined using the spin–echo pulse sequence shown in Fig. 1. The initial 90° pulse generated the free induction decay (FID) signal and its measurement at $50 \mu\text{s}$ following the 90° pulse gave the total hydrogen nuclei signal amplitude S_{Total} consisting of lipid and moisture as signal from the solid starch molecules (relaxation rates in the 7.1 – $10.1 \mu\text{s}$ range) have decayed (Choi and Kerr, 2003). The S_{Lipid} amplitude at 7 ms is proportional to the quantity of lipid components in the composite and the delay (τ) of 3.5 ms before application of the 180° pulse is sufficiently long to eliminate refocusing of signals due to water. The moisture content of the composites was then found by difference in amplitudes between S_{Total} and S_{Lipid} .

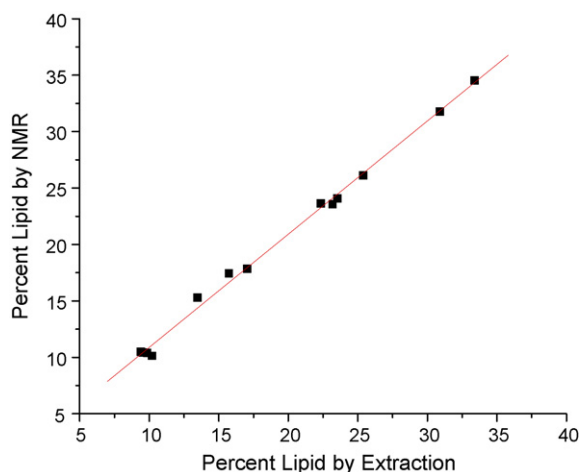


Fig. 3. Correlation between the lipid content in 13 starch–lipid composites samples determined by TD-NMR (spin–echo pulse) measurement and hydrolysis/extraction methodology. The correlation coefficient was 0.998.

As shown in Table 1 (column 4), the percentage of SBO or BF in the various composites determined from the spin–echo TD-NMR experiments agreed well to the lipid percentages determined from the starch hydrolysis/extraction experiments (Table 1, column 3). Fig. 3 shows the correlation between the lipid contents for the 13 starch–SBO and starch–BF composite samples determined by spin–echo TD-NMR and the α -amylase digestion/extraction method. As can be seen, a high correlation was observed between the two methods used to determine the lipid content ($R^2 = 0.998$) in the composites. The regression line had a slope of 1.003 and an intercept of 0.8538.

The moisture content determined by spin–echo TD-NMR (Table 1, column 6) was found to be in fair agreement to the moisture levels determined by freeze-drying for the composites. Fig. 4 graphically depicts the moisture data determined by TD-NMR and by freeze-drying. The regression line had a slope of 0.8220 and an intercept of 1.0846 with an $R^2 = 0.881$. The lower correlation between the TD-NMR and freeze-drying results for moisture as compared to the lipid correlation underscores the inherent difficulties surrounding the accurate determination of moisture as pointed out by others (Rückold et al., 2001; Thiex and Richardson, 2003). From our results, the freeze-drying method utilized may not have entirely dehydrated the composite samples and TD-NMR calibration curves based upon these gravimetric composite moistures may have led to the lower correlation between the NMR and freeze-drying composite moistures. We briefly examined

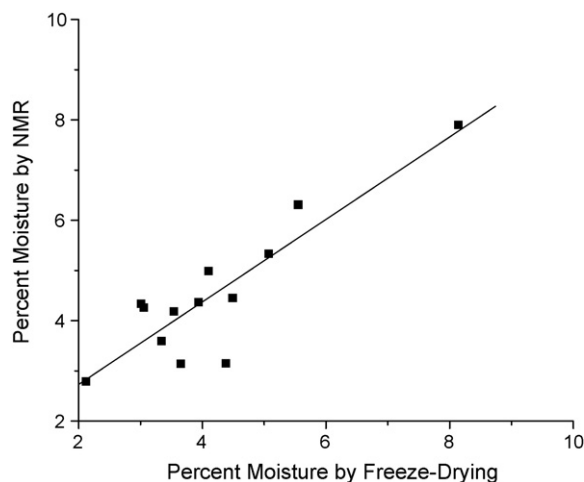


Fig. 4. Correlation between the moisture content in 13 starch–lipid composites samples determined by gravimetrically by freeze-drying and TD-NMR (spin–echo pulse) measurement. The correlation coefficient was 0.881.

methods based on the use of vacuum oven and a moisture analyzer drying to obtain water contents of the composites but found these methods to be less reproducible as lipid volatiles are more likely to be removed using these methods.

4. Conclusions

In addition to being rapid and non-invasive, the TD-NMR technique has been shown to be a useful tool to accurately quantitate the amount of oil in the starch–lipid composites. Our extraction results show that starch–lipid composites with well defined lipid amounts can be prepared, and the excellent correlation of lipid amounts between the TD-NMR and extraction techniques shows TD-NMR is an excellent method to characterize the oil content within the starch–lipid composites. By using a spin–echo pulse sequence the amount of moisture contained in the starch–lipid composites can also be evaluated simultaneously when appropriate calibration standards are utilized. The initial CPMG experiments provide insight into the interactions between the different components present in these composites.

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References

- Biresaw, G., Kenar, J.A., Kurth, T.L., Felker, F.C., Erhan, S.M., 2007. Investigation of the mechanism of lubrication in starch–oil composite dry film lubricants. *Lubr. Sci.* 19, 41–55.
- Byars, J., 2002. Effect of a starch–lipid fat replacer on the rheology of soft-serve ice cream. *J. Food Sci.* 67, 2177–2182.
- Choi, S.G., Kerr, W.L., 2003. Water mobility of textural properties of native and hydroxypropylated wheat starch gels. *Carbohydr. Polym.* 51, 1–8.
- D'Avignon, D.A., Hung, C., Pagel, M.T.L., Hart, B., Bretthorst, G.L., Ackerman, J.J.H., 1990. ^1H and ^2H NMR studies of water in work-free wheat flour doughs. In: Finley, J.W., Schmidt, S.J., Serianni, A.S. (Eds.), *NMR Applications in Biopolymers*. Plenum Press, New York, pp. 391–414.
- Eskins, K., Fanta, G.F., 1997. Non-separable starch–oil compositions. U.S. Patent 5,676,994.
- Eskins, K., Fanta, G.F., 1999. Non-separable compositions of starch and water-immiscible organic materials. U.S. Patent 5,882,713.
- Eskins, K., Fanta, G.F., Felker, F.C., Baker, F.L., 1996. Ultrastructural studies on microencapsulated oil droplets in aqueous gels and dried films of a new starch–oil composite. *Carbohydr. Polym.* 29, 233–239.
- Fanta, G.F., Eskins, K., 1995. Stable starch–lipid compositions prepared by steam jet cooking. *Carbohydr. Polym.* 28, 171–175.
- Fanta, G.F., Felker, F.C., Eskins, K., Baker, F.L., 1999. Aqueous starch–oil dispersions prepared by steam jet cooking. Starch films at the oil–water interface. *Carbohydr. Polym.* 39, 25–35.
- Gambhir, P.N., 1992. Applications of low-resolution pulsed NMR to the determination of oil and moisture in oilseeds. *Trends Food Sci. Technol.* 3, 191–196.
- Garzon, G.A., McKeith, F.K., Gooding, J.P., Felker, F.C., Palmquist, D.E., Brewer, M.S., 2003. Characteristics of low-fat beef patties formulated with carbohydrate–lipid composites. *J. Food Sci.* 68, 2050–2056.
- Hickey, H., MacMillan, B., Newling, B., Ramesh, M., Van Eijck, P., Balcom, B., 2006. Magnetic resonance relaxation measurements to determine oil and water content in fried foods. *Food Res. Int.* 29, 612–618.
- Klem, R.E., Brogley, D.A., 1981. Methods for selecting the optimum starch binder preparation system. *Pulp Paper* 55, 98–103.
- Knutson, C.A., Eskins, K., Fanta, G.F., 1996. Composition and oil-retaining capacity of jet-cooked starch–oil composites. *Cereal Chem.* 73, 185–188.
- Leung, H.K., Magnuson, J.A., Bruinsma, B.J., 1983. Water binding of wheat flour doughs and breads as studied by deuterium relaxation. *J. Food Sci.* 48, 95–99.
- Meiboom, S., Gill, D., 1958. Modified spin–echo method for measuring nuclear relaxation times. *Rev. Sci. Instrum.* 29, 688–691.
- Ruan, R.R., Chen, P.L., 1998. Rapid determination of moisture contents in food and biological materials. In: Ruan, R.R., Chen, P.L. (Eds.), *Water in Foods and Biological Materials. A Nuclear Magnetic Resonance Approach*. Technomic Publishing Co., Lancaster, pp. 75–93.
- Rubel, G., 1994. Simultaneous determination of oil and water contents in different oilseeds by pulsed nuclear magnetic resonance. *J. Am. Oil Chem.* 71, 1057–1062.
- Rückold, S., Grobecker, K.H., Isengard, H.-D., 2001. Water as a source of errors in reference materials. *Fresenius J. Anal. Chem.* 370, 189–193.

- Srinivasan, V.T., 1979. A comparison of different pulse sequences in the nondestructive estimation of seed oil by pulsed nuclear magnetic resonance technique. *J. Am. Oil Chem. Soc.* 56, 1000–1003.
- Thiex, N., Richardson, C.R., 2003. Challenges in measuring moisture content of feeds. *J. Anim. Sci.* 81, 3255–3266.
- Todt, H., Burk, W., Guthausen, G., Guthausen, A., Kamlowski, A., Schmalbein, D., 2001. Quality control with time-domain NMR. *Eur. J. Lipid Sci. Technol.* 103, 835–840.
- Todt, H., Guthausen, G., Burk, W., Schmalbein, D., Kamlowski, A., 2006. Water/moisture and fat analysis by time-domain NMR. *Food Chem.* 96, 436–440.